

# Multi-Ion Coincidence Measurements of Methyl Chloride Following Photofragmentation Near the Chlorine *K*-Edge

D. L. Hansen,<sup>1</sup> J. Cotter,<sup>2</sup> G. R. Fisher,<sup>3</sup> K. T. Leung,<sup>4</sup> R. Martin,<sup>1</sup> P. Neill,<sup>2</sup> R. C. C. Perera,<sup>3</sup> M. Simon,<sup>5,6</sup> Y. Uehara,<sup>7</sup> B. Vanderford,<sup>1</sup> S. B. Whitfield,<sup>8</sup> and D. W. Lindle<sup>1</sup>

<sup>1</sup>Department of Chemistry, University of Nevada, Las Vegas, NV 89154-4003

<sup>2</sup>Department of Physics, University of Nevada, Reno, NV 89557-0058

<sup>3</sup>E. O. Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720, USA

<sup>4</sup>Department of Chemistry, University of Waterloo, Canada, N2L 3G1

<sup>5</sup>LURE, Bâtiment 209D, Université Paris-Sud, 91405 Orsay Cedex, France

<sup>6</sup>CEA/DRECAM/SPAM, Bâtiment 522, CEN Saclay, 91191 Gif/Yvette Cedex, France

<sup>7</sup>Mitsubishi Electric Corporation, Amagasaki, Hyogo, 661 Japan

<sup>8</sup>Department of Physics and Astronomy, University of Wisconsin, Eau Claire, WI 54702

## INTRODUCTION

Multi-ion coincidence techniques, often referred to as charge-separation mass spectroscopy (CSMS)[1], provide a powerful experimental tool for the determination of the dissociation dynamics of photoexcited molecules. Detection of several positively charged fragments from a single dissociation event allows differentiation among specific processes when a multitude of decay paths are possible, simplifying characterization of the photofragmentation mechanism. Synchrotron radiation (SR) is an excellent excitation source for these types of measurements because it is readily made both tunable and monochromatic. Using x-ray SR, it is possible to excite a core electron localized around a specific atom in a molecule, providing a chemical-site specific probe. By localizing the initially excited state, it is possible to determine if site-selective-fragmentation effects, where the fragmentation pathways change as a result of excitation of electrons from chemically different sites, are present [2]. Both extremes for site selectivity exist, where either the decay pathway is dependent on the location of the initial excitation [3-4], or where the system has no memory of the initially excited state [5-6].

Relaxation dynamics of  $\text{CH}_3\text{Cl}$  following core-shell photoexcitation in the neighborhood of the chlorine *K* edge ( $\approx 2.8$  keV) was studied via multi-ion coincidence measurements using a time-of-flight

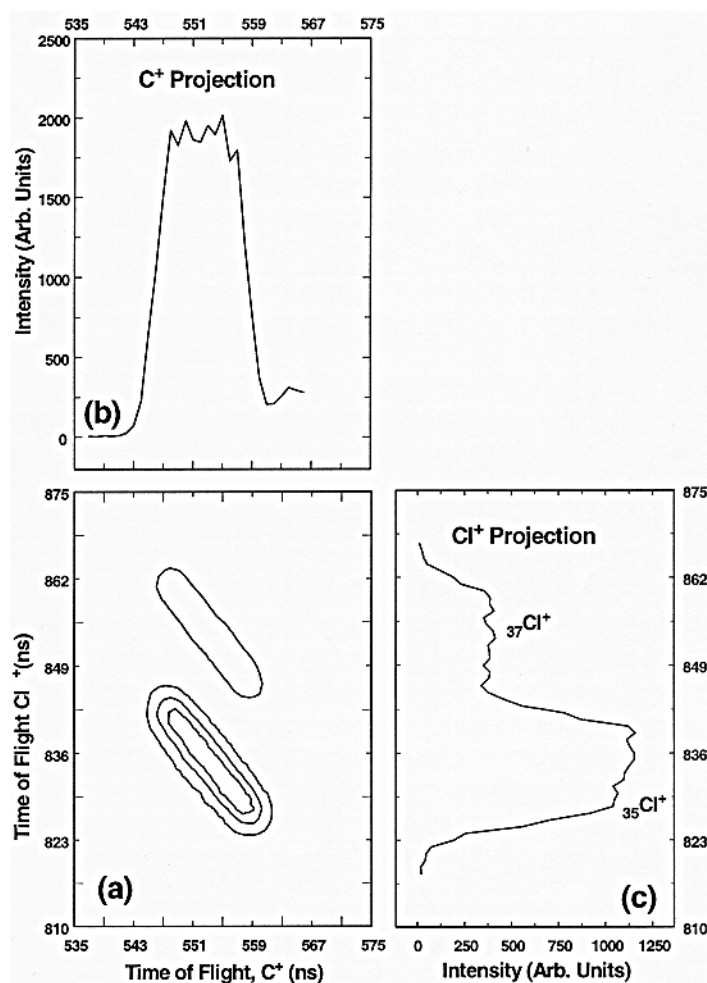


Figure 1. Projection of the coincident triplet ( $\text{H}^+$ ,  $\text{C}^+$ ,  $\text{Cl}^+$ ) onto the (a)  $\text{C}^+$  -  $\text{Cl}^+$  plane, (b) the  $\text{C}^+$  TOF axis, (c) the  $\text{Cl}^+$  TOF axis.

mass spectrometer. The data provide evidence for sequential fragmentation moderated by Coulombic interactions among the fragments. The sequential nature of the fragmentation indicates that chemical forces, especially between the carbon and chlorine atoms, are dominant in determining the kinematics of the fragmentation. This is especially true on resonance where fast dissociation is observed following electron excitations to the  $8a_1$  antibonding orbital.

## EXPERIMENT

The experiments were performed using x-ray synchrotron radiation from beamline 9.3.1 at the Advanced Light Source (ALS)[7-9]. This beamline provides a flux of  $10^{11}$  photons  $s^{-1}$  in a bandpass  $\leq 0.5$  eV. An ion-time-of-flight (TOF) mass spectrometer [10] oriented with its axis parallel to the polarization vector of the incident SR, was used to detect ions created following x-ray absorption. The gas under study is supplied effusively by a grounded needle centered between two stainless-steel plates held at equal but opposite voltages. The ions created via x-ray absorption traverse a series of regions with different electric-field strengths until they are detected by a pair of microchannel plates.

For  $CH_3Cl$ , spectra were collected at photon energies in the vicinity of the  $K$ -shell ionization threshold with three levels of complexity. “Singles” spectra were collected using an electronic setup described previously [10]. A time-to-amplitude converter (TAC) measures the time difference between the detection of a single ion and the subsequent ring-timing pulse, thus flight times are inverted relative to the mass-to-charge ratio. Only one ion is detected for each fragmentation event and the data are recorded as the number of counts versus flight time. For “doubles” and “triples” spectra, a PC-based, multi-stop, time-to-digital converter (TDC) acts as a nanosecond stopwatch to record ion flight times. The ring timing signal is used to start the TDC, and detection of an ion is used to stop it. However, because the frequency of the ring-timing signal ( $\approx 3$  MHz) is much greater than the ion count rate, it is necessary to use a logic circuit to reduce the amount of dead time from TDC starts with no corresponding stops. For doubles and triples spectra, two or three ions are detected following a single fragmentation event; doubles data record flight times for two ions ( $t_1$ ,  $t_2$ , counts), while triples data record flight times for three ions ( $t_1$ ,  $t_2$ ,  $t_3$ , counts). Figure 1 shows data collected for the coincidence triplet ( $H^+$ ,  $C^+$ ,  $Cl^+$ ). In the figure, the three dimensional coincidence volume is projected

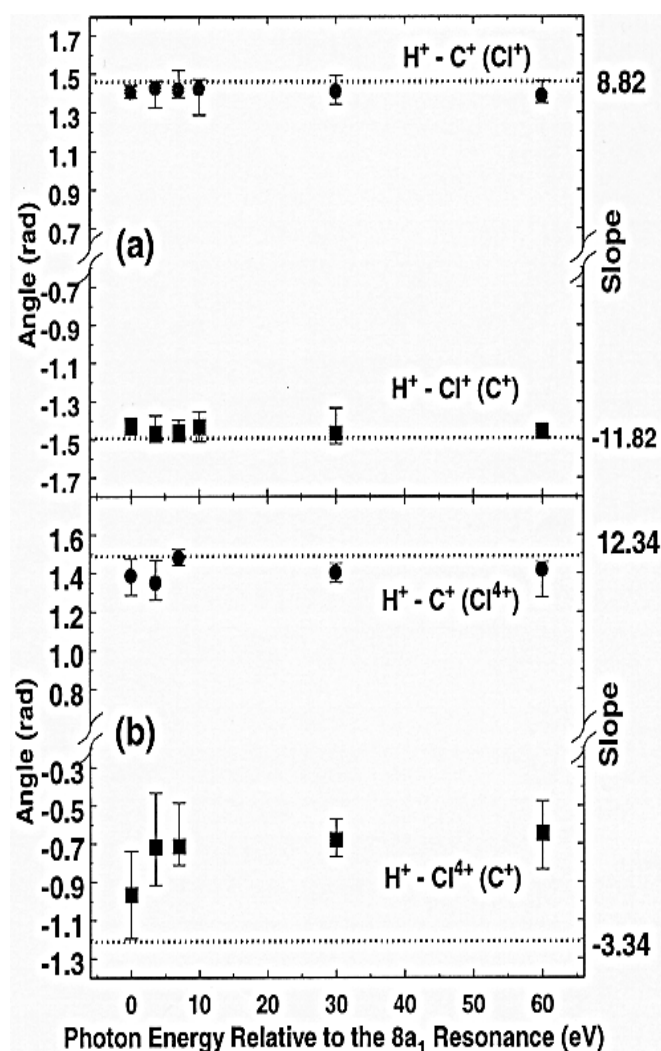


Figure 2. Slopes of contour plots produced by projection of coincidence volumes onto planes defined by the ion time of flight axes.

onto a plane [Fig. 1(a)] and the axes [Fig. 1(b)-(c)] defined by the flight times of the second and third ions respectively. Because of the information it contains on the momentum released in the fragmentation process, the most important parameter in determining fragmentation mechanisms from multi-ion coincidence measurements is the slope of the coincidence peak [1]. This is determined from contour plots such as Fig. 1(a) created when a coincidence volume is projected onto one of the three different planes defined by the ion flight times. For a molecule such as  $\text{CH}_3\text{Cl}$ , the slopes of the coincidence peaks will allow differentiation between deferred charge separation (DCS) mechanisms, where a neutral fragment is ejected in the first step of dissociation; secondary decay (SD), where a neutral is ejected in the second step of dissociation; and concerted dissociation (CD) processes where all fragments separate simultaneously.

Figure 2(a) shows that for singly charged ions ( $\text{C}^+$ ,  $\text{Cl}^+$ ) measured in coincidence with  $\text{H}^+$  there appears to be little or no change in slope, and thus dissociation mechanism, as a function of energy. The slopes also appear to agree well with calculated values. However the situation is different for more highly charged ions [Fig 2(b)]. The slopes of the  $\text{H}^+$  -  $\text{Cl}^{4+}$  clearly change in the first few eV above resonance, and show better agreement with the calculated values on resonance. Looking at the widths of the chlorine peaks as a function of energy (Fig. 3) indicates that for all charge states, there is a greater amount of energy released in fragmentation on resonance than at energies above resonance. A likely explanation is, on resonance, the excitation of the core electron into the  $8a_1$  antibonding orbital initiates the C-Cl bond rupture, consequently, the electrostatic repulsion introduced by population of an antibonding orbital causes a more energetic ejection of the chlorine ion in a manner analogous to the fast dissociation observed for resonant excitation of  $\text{HCl}$  [11]. Because of this, the chlorine ion has less Coulombic interaction with the other ions, the fragmentation is more sequential, and the slopes of coincidence peaks show better agreement with the values calculated using the sequential model. In addition, for all ionic triplets, the FWHM for the  $\text{H}^+$  ions (not shown) are consistently narrower on resonance, as would be expected in the case of a reduced Coulombic interaction. In contrast, upon excitation to Rydberg orbitals (3.4 eV above resonance) or to the continuum (5 eV above resonance), rupture of the C-Cl bond results solely from electronic depletion following Auger decay. In addition, with the higher ionic charge states inherent to above-threshold energies comes greater mutual repulsion between the ions, making fragmentation a more concerted process and changing the slope. These results suggest that by using multi-ion-coincidence techniques it is in principle possible to determine an upper bound for the energy of electrostatic repulsion arising from excitations to the  $8a_1$  antibonding orbital, and to use this information to map out the potential curves for different fragmentation

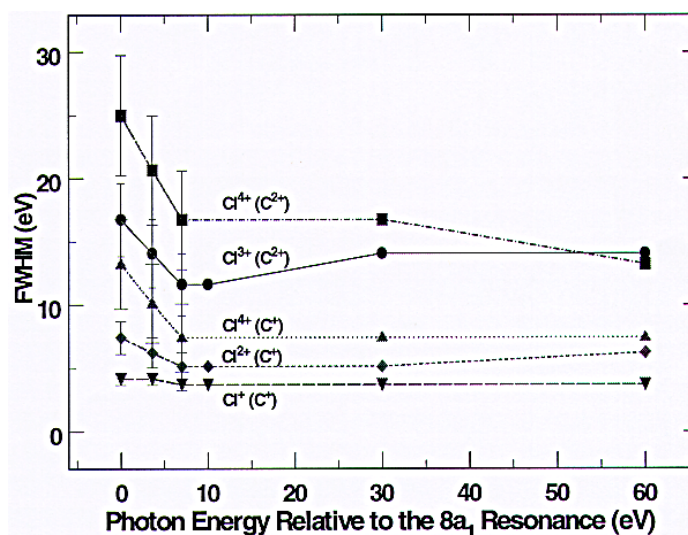


Figure 3. FWHM of chlorine ion peaks versus photon energy. Squares (■) represent the FWHM of  $\text{Cl}^{4+}$  measured in coincidence with  $\text{H}^+$  and  $\text{C}^{2+}$ . Circles (●) FWHM of  $\text{Cl}^{3+}$  measured in coincidence with  $\text{H}^+$  and  $\text{C}^{2+}$ . Up triangles (▲) FWHM of  $\text{Cl}^{4+}$  measured in coincidence with  $\text{H}^+$  and  $\text{C}^+$ . Diamonds (◆) FWHM of  $\text{Cl}^{2+}$  measured in coincidence with  $\text{H}^+$  and  $\text{C}^+$ . Down triangles (▼) FWHM of  $\text{Cl}^+$  measured in coincidence with  $\text{H}^+$  and  $\text{C}^+$ .

pathways. However, because a large extraction voltage was used in these experiments, the resolution for the kinetic energy of the fragments is poor, and it is difficult to derive any quantitative results.

In conclusion, the fragmentation dynamics of  $\text{CH}_3\text{Cl}$  were studied using triple-coincidence CSMS methods. By measuring the slopes of different coincidence maps, and looking at the FWHM of the different ions, it is found that a sequential decay mechanism, initiated by the rupture of the C-Cl bond, describes the dissociation process well for all ionic charge states, and that the process is moderated by Coulombic interaction among the particles. In addition, an increase in the FWHM on resonance, combined with better agreement of the slopes of the more highly charged chlorine ions with the calculated values was attributed to fast dissociation caused by the electrostatic repulsion following excitation of a core electron to the  $8a_1$  antibonding orbital. The sequential dissociation as well as the additional electrostatic repulsion following resonant excitation provide strong evidence that chemical forces are the dominant factor governing the kinematics of the fragmentation, and that Coulombic repulsion plays a subordinate role in the dissociation.

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Principal investigator: Dennis Lindle, Department of Chemistry, University of Nevada, Las Vegas. Email: lindle@nevada.edu. Telephone: 702-895-4426.